

## DIRECT REDUCTION OF METALLIC ORES

Patent number: GB1471544  
Publication date: 1977-04-27  
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Classification:  
- International: C21B13/00; C21B15/00; C22B5/10; C21B13/00;  
C21B15/00; C22B5/00; (IPC1-7): C21B13/00;  
C22B15/00; C22B23/02  
- European: C21B13/00F; C21B13/00P; C21B15/00; C22B5/10  
Application number: GB19740046305 19741025  
Priority number(s): GB19740046305 19741025

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### Abstract of **GB1471544**

1471544 Direct reduction of ores BRITISH STEEL CORP and UNIVERSITY OF STRATHCLYDE 24 Oct 1975 [25 Oct 1974] 46305/74 Heading C7D In a process for the direct reduction of metallic ores, the particulate ore is mixed with a nucleating agent and an agent to promote activity of the reducing agent. In the case of iron ore, both the nucleating agent and the activating agent are  $FeCl_3$ , the iron ore being magnetite or hematite and the reducing agent powdered coal, coke or graphite. The reduction of Cu and Ni oxides is also referred to. Other examples of activating agents are the halides, nitrates, carbonates, oxides and organic compounds of Fe, Ni, Co, Na, and Li; alternative nucleating agents are Fe, Ni, Co, and Cu compounds, especially halides, e.g.  $CuCl_2$  for Cu ores,  $NiCl_3$  for Ni ores. Hydrides or organic compounds may also be added to produce  $H_2$ . In an example a mixture of particulate magnetite,  $FeCl_3$  and  $H_2O$  was thoroughly mixed with a mixture of particulate coal,  $FeCl_3$  and  $H_2O$ ; the pellets produced were dried, purged with cold  $N_2$ , heated slowly in heated  $N_2$  to 1050 C in a retort, held for 30 minutes, cooled in a cold  $N_2$  stream and discharged, giving a 98% metallization.

### Also published as:

 JP51066215 (A)  
 DE2547574 (A1)

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# PATENT SPECIFICATION

(11) 1 471 544

1 471 544

(21) Application No. 46305/74 (22) Filed 25 Oct. 1974  
 (23) Complete Specification filed 24 Oct. 1975  
 (44) Complete Specification published 27 April 1977  
 (51) INT CL<sup>2</sup> C21B 13/00 C22B 15/00 23/02  
 (52) Index at acceptance  
 C7D 14A3B 24 5K6 5L5 5M3 5N12 5N13 5N1 5N5 5N6  
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## (54) DIRECT REDUCTION OF METALLIC ORES

(71) We, BRITISH STEEL CORPORATION, a Corporation incorporated and existing under the Iron & Steel Act 1967 of 33 Grosvenor Place, London, S.W.1., England, and THE UNIVERSITY OF STRATHCLYDE of Colville Buildings, Richmond Street, Glasgow, Scotland, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the direct reduction of metallic ores. The reduction of iron ore using graphite has been previously proposed (see British Patent No. 1,246,308).

We have now discovered that the rate of direct reduction of metallic ores such as iron ore using a finely divided reducing agent such as carbon in the form of coal or coke or graphite can be increased enormously by mixing a nucleating agent (which could be ferric chloride in the case of iron ore) with the metallic ore to nucleate metal on the surface of the ore and using an activator to promote activity of the carbon. The activator may also be ferric chloride, although it may be other substances which deposit iron or other metal atoms or compounds on the carbon surface. Even in an inert bulk gas atmosphere the rate of reduction can be increased as much as tenfold and also the temperatures at which significant reduction can be achieved is considerably lowered.

In the reduction of iron oxide, by use of this invention we prefer to use ferric chloride both as a nucleating agent for the iron and to increase the activity of the carbon. The ferric chloride may be mixed with the carbon and iron oxide separately or simultaneously.

One specific example of the method in accordance with the invention will now be described:

1 tonne of magnetite ore (Malmberget Superconcentrate) of particle size 75% less than 45 micron, 100% less than 200 micron

was pug-mixed with a solution/slurry containing 100 kg of FeCl<sub>3</sub> and 80 kg H<sub>2</sub>O.

300 kg Yorkshire coal (84.5% carbon) of the same particle size distribution was pug-mixed with a solution/slurry containing 30 kg FeCl<sub>3</sub> and 24 kg H<sub>2</sub>O.

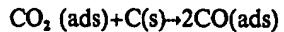
The two mixtures were then thoroughly pug-mixed together and fed to a balling disc where the final moisture addition (26 kg) to effect the balling was added as a fine spray. The balls in the size range 9—16 mm were dried in a tray dryer.

The balls were then transferred to a retort, purged with cold nitrogen and heated slowly by means of heated nitrogen to 1050°C, held for 30 minutes, cooled in a stream of cold nitrogen and discharged. 98% metallisation was observed to take place.

The CO product of the reaction between iron ore and carbon was used in part to fire the recuperator heating the nitrogen supply. Fresh nitrogen was passed through the heater by means of a blower.

Using this method the reduction of iron ore by coal in a neutral bulk gas atmosphere can be achieved in the same time as reduction with carbon monoxide at one atmosphere pressure with pellets of the same size. In place of the magnetite ore used in the example, hematite may be used.

The mechanism of the fast reduction reaction has been found to be one of a localised gas transfer reaction. CO<sub>2</sub> gas, formed initially from reaction of the carbon in direct contact with the oxide, is adsorbed at the 'activated' coal surface where the reaction



takes place. Two molecules of CO are then available for further reduction of the iron oxide. CO molecules are not readily adsorbed at the wustite surface however and the adsorption reaction will only proceed rapidly when iron is present at the surface of the particle. The use of a nucleating agent ensures the presence of

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nucleated metal on the surface of the ore. Oxygen atoms from the FeO then diffuse to the iron layer and to the adsorbed CO molecules, the reaction proceeds and CO<sub>2</sub> is formed. Subsequent reduction of CO<sub>2</sub> to CO again occurs giving rise to a cataclysmic reduction reaction. It is essential that the iron is in intimate contact with the wustite layer since oxygen transfer from the oxide phase would not occur readily. On the basis of this theory the high reduction rate of iron oxides with graphite in neutral atmospheres is achieved when a sufficient build up of CO and CO<sub>2</sub> gases occurs within the localised atmosphere between the carbon and oxide particles. At low carbon reactivities this critical condition may never be reached since the gases will have time to escape from the sample.

Another way in which the invention could be effected is to use hydrides or organic compounds to produce hydrogen, initiating the reduction; ferric chloride or nickel chloride being used as a nucleating agent.

Other carbon activators mainly in the form of a metallic elements may be added to the carbon in the form of organic compounds, halides, nitrates, carbonates and oxides. Examples of such carbon activators that may be employed are iron, nickel, cobalt, sodium and lithium.

In addition to ferric chloride, nickel, cobalt and copper compounds especially their halides can be used as nucleating agents on the iron oxide.

In place of iron ore, other metal oxides may be used such as nickel, copper oxide etc. in which case the nucleating agent would preferentially be the corresponding halide, e.g. nickel chloride and cupric chloride.

The use of coal in the process offers some inherent advantages in that it contains volatile compounds in addition to carbon; these volatile compounds offer the possibility of assisting the initiation of the fast reduction reaction. Catalysed iron-magnetite powders containing 10 w/o FeCl<sub>3</sub>, heated at 950°C produce reduction of in excess of 95% of the oxide. This contrasts with a maximum of 80% metallization achieved in the uncatalysed samples under the same conditions, in addition reaction rates in the catalysed samples are significantly increased by the additives.

The major advantage of the present technique is that the overall reaction rate is dependent on the particle size of the ore and will be independent of the pellet size. This factor is particularly important when large pellets are to be used and the only limitation which appears to be significant at present is heat transfer to the centre of the pellets. The temperature at which the reduction reaction is carried out also provides for limited sintering of the iron and the final pellet strength will be dictated by the reaction time and particle sizes of the components in addition to initial preparation conditions.

One particular application of the process is in the production of pre-reduced pellets for subsequent utilisation in electric arc steelmaking.

WHAT WE CLAIM IS:—

1. A process of direct reduction of metallic ores in which a nucleating agent is mixed with the metallic ore to nucleate metal on the surface of the ore and an activator is used to promote activity of the reducing agent.
2. A process according to claim 1 and in which the metallic ore is iron ore and the nucleating agent is ferric chloride.
3. A process according to claim 1 or claim 2 and in which the activator is ferric chloride.
4. A process according to any preceding claim and in which both the activator and the nucleating agent are ferric chloride and the ferric chloride is mixed with the reducing agent and the metallic ore separately.
5. A process according to any preceding claim and in which the iron ore is in the form of magnetite powder.
6. A process according to any preceding claim and in which the reducing agent is in the form of carbon.
7. A process according to claim 6 and in which the carbon is coal in particulate form.
8. A process of direct reduction as claimed in claim 1 and substantially as hereinbefore particularly described.

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